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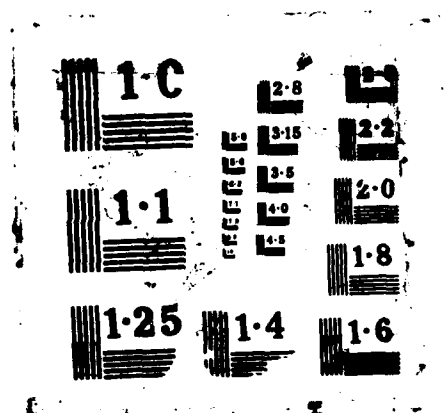
AN ABSOLUTE SCANNING (NF (ALPHA (1DELTA)) AND (NF
(B(1EPSILON)) DIAGNOSTIC FOR THE N2F4 + H2 SYSTEM(U)
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AN ABSOLUTE SCANNING [NF ($\alpha^1\Delta$)] AND
[NF ($b^1\Sigma$)] DIAGNOSTIC FOR THE $N_2F_4 + H_2$
SYSTEM

Y. D. Jones

June 1987

Final Report



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AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base, NM 87117-6008

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The N ₂ F ₄ + H ₂ system is of interest for production of NF(a ¹ Δ) as an energy transfer species. Past studies have been plagued with the difficult NF(a ¹ Δ) quantitative measurement due to interferences from the close-lying N ₂ (B) and HF peaks. This paper deals with the development of a scanning diagnostic to determine concentrations of NF(a ¹ Δ) and NF(b ¹ Σ) in the N ₂ F ₄ + H ₂ system and quantitative measurement of interferences with the diagnostic signal. The diagnostic was then applied to a functioning high-pressure, high-temperature system.					
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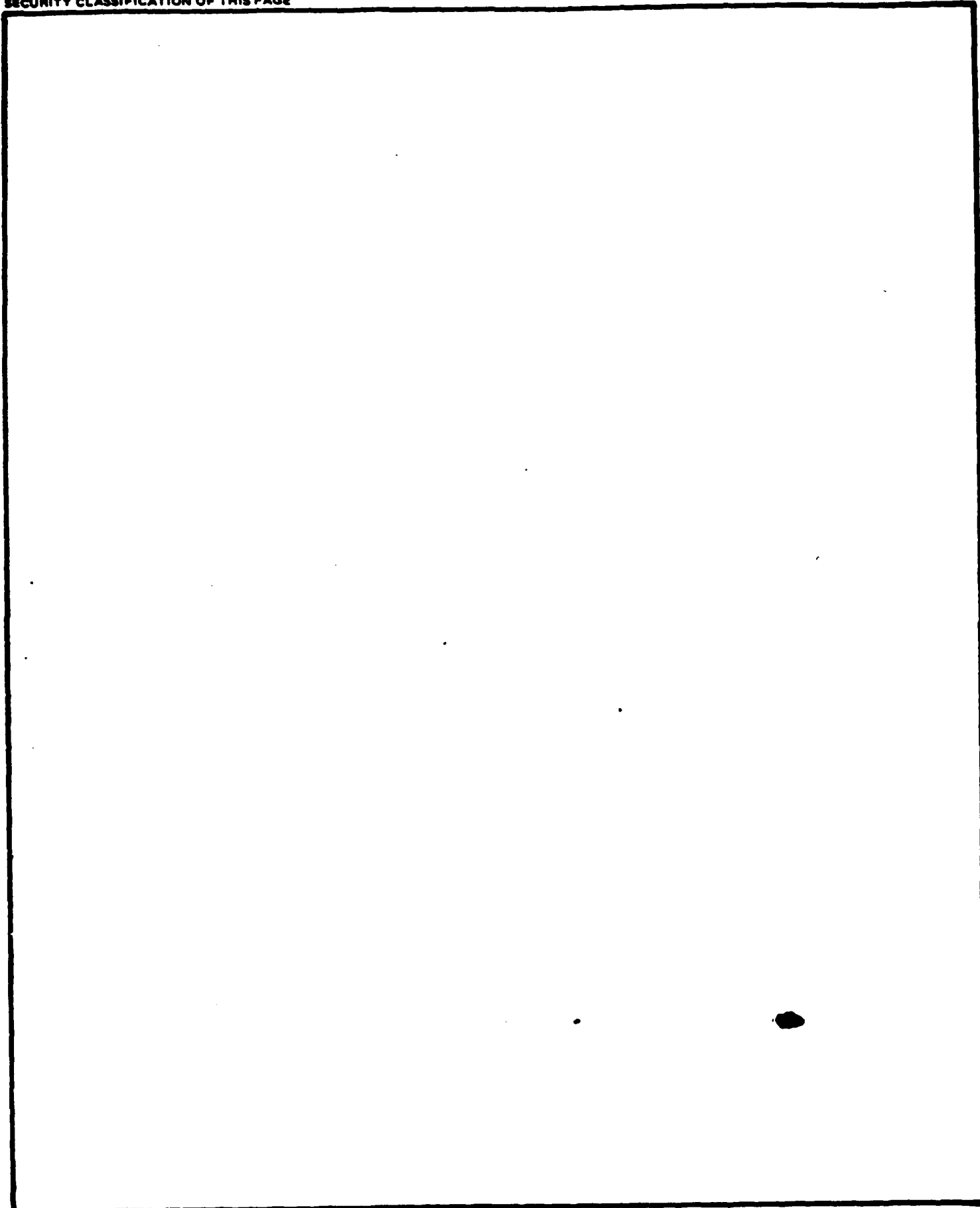
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ILLUSTRATIONS

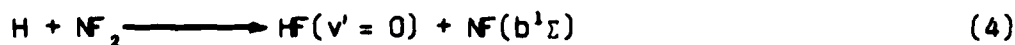
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I. INTRODUCTION

The $N_2F_4 + H_2$ chemical production scheme for $NF(a^1\Delta)$ and $N_2(A)$ is of interest because of the large amount of energy stored in both molecules. The $NF(a^1\Delta)$ concentration in these systems has been difficult to determine due to the close-lying peaks of the $N_2(B)$ and HF spectra. This report describes reliable $NF(a^1\Delta)$ and $NF(b^1\Sigma)$ diagnostics. The $N_2(B)$ and HF interferences in our system have been identified and quantified. These studies have provided an accurate method of determining $NF(a^1\Delta)$ in high densities, as well as $NF(b^1\Sigma)$ in moderate concentrations.

The $NF(a^1\Delta)$ molecule is long-lived at 5.6 seconds (Ref. 1) and has an internal energy of 11500 cm^{-1} available for transfer. $NF(b^1\Sigma)$, also produced in this system, has a lifetime of 23 ms (Ref. 2). The $NF(a)$ and $NF(b)$ states were detected using spontaneous emission detection by absolute radiometry. The $NF(a^1\Delta) \rightarrow NF(X^3\Sigma)$ at 874.2-nm transition and the $NF(b^1\Sigma) \rightarrow NF(X^3\Sigma)$ at 528.8-nm transition were used to monitor the concentrations in a supersonic flow regime.

The reactions in the $N_2F_4 + H_2$ system leading to $NF(a^1\Delta)$ and $NF(b^1\Sigma)$ are summarized in Eqs. 1 through 5.



1. Malins, R. J., and D. W. Senser, J. Chem. Phys. **85**, 1342 (1981).
2. Cheah, C. T., and M. A. A. Clyne, J. Photochem. **15**, 21 (1981) and P. H. Tennyson, A. Fontijn, and M. A. A. Clyne, J. Chem. Phys. **62**, 171 (1981).

The diagnostic was incorporated in the study of the overall $\text{N}_2\text{F}_4 + \text{H}_2$ production scheme for N_2^+ . The operating regime for the diagnostic was detection of high densities in supersonic, high-temperature flows. The device and additional diagnostics will be described in a future report.

II. DESIGN

The diagnostic incorporated a 0.953-cm-diam tube, 38.1 cm long. Both ends were fitted with 0.17-cm-diam orifices held in place by tubing fittings. A bifurcated fused silica fiber optic cable (Oriel) was fixed in the fitting on one end of the tube. The tube or spatial filter was then attached to a translation stage. The position of the translation stage, and thus the spatial filter, was determined from the output from a calibrated linear voltage displacement transducer (LVDT).

The setup for the diagnostics is shown in Figure 1. The $NF(a^1\Delta)$ emission was detected by a thermoelectrically cooled RCA C31034A photomultiplier tube (PMT) which was attached to one of the bifurcated cable ends. Between the fiber optic and the PMT was a very narrow band-pass filter (Barr Associates) centered at 874.29 nm with a full width at half maximum (FWHM) of 0.98 nm. Maximum transmission was 0.52. The $NF(b^1\Sigma)$ was detected by emission passing through the other side of the cable, a band-pass filter (Corion) centered at 531.4 nm with a FWHM of 9.8 nm and maximum transmission of 0.54, and to a thermoelectrically cooled RCA 4837 PMT. Each PMT was optimized for response with regard to both voltage applied and temperature of the cooled housing.

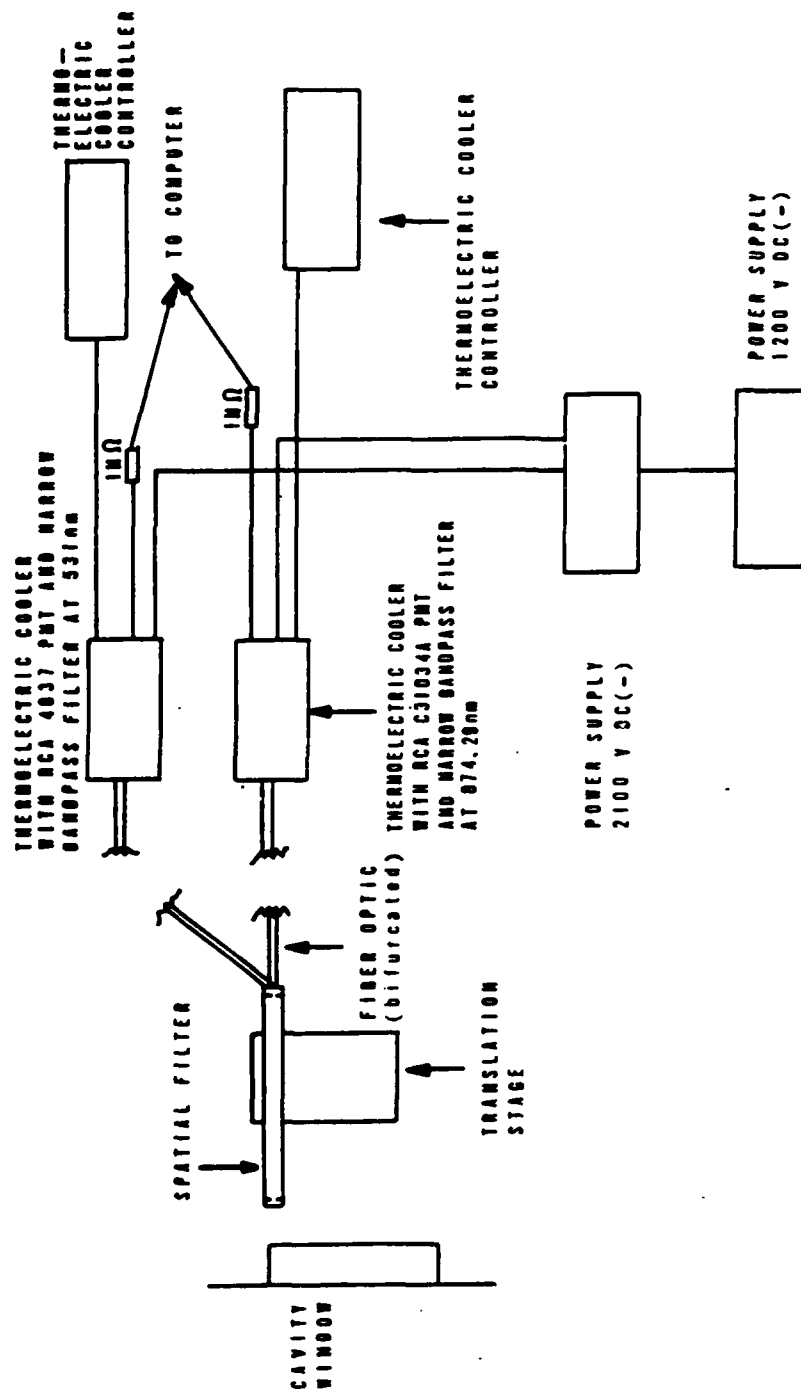


Figure 1. Schematic of the NF(a¹Δ) and the NF(b¹Σ) diagnostics.

III. CALIBRATION

STANDARD LAMP CALIBRATION

Calibration of the diagnostics was performed using a quartz-halogen-tungsten FEL-type lamp, the calibration of which was performed with an NBS standard (Eppley Laboratory, Inc.). The lamp was periodically checked in-house against an NBS secondary standard. The lamp was run at 7.9 A.

The calibration procedure and geometry considerations have been previously described (Ref. 3). To summarize, the differential radiated power, dP , which reaches the rear aperture of the spatial filter is given by

$$dP = [NF^*] h\nu k_T \frac{f(r, z) A \cos\theta}{4\pi(r^2 + z^2)} dV \quad (6)$$

where

$[NF^*]$ = molecules/cm³ of either NF(a¹Δ) or NF(b¹Σ)

$h\nu$ = Energy of a photon at the emission frequency

k_T = Radiative rate of the transition

A = Rear aperture area (cm²)

$\frac{f(r, z) A \cos\theta}{4\pi(r^2 + z^2)}$ = Solid angle subtended at the rear aperture by the differential volume element with radius = $(r^2 + z^2)^{1/2}$

θ = angle between the z-axis and the radius vector that connects the origin to the differential volume element

$f(r, z)$ = occlusion factor

Figure 2 shows the experimental arrangement of the diagnostic. The shape of the flame was monitored via a video camera and digitized to determine the

3. Johnson, D., R. Meyer, Y. D. Jones and G. Hager, Laser Digest, to be published.

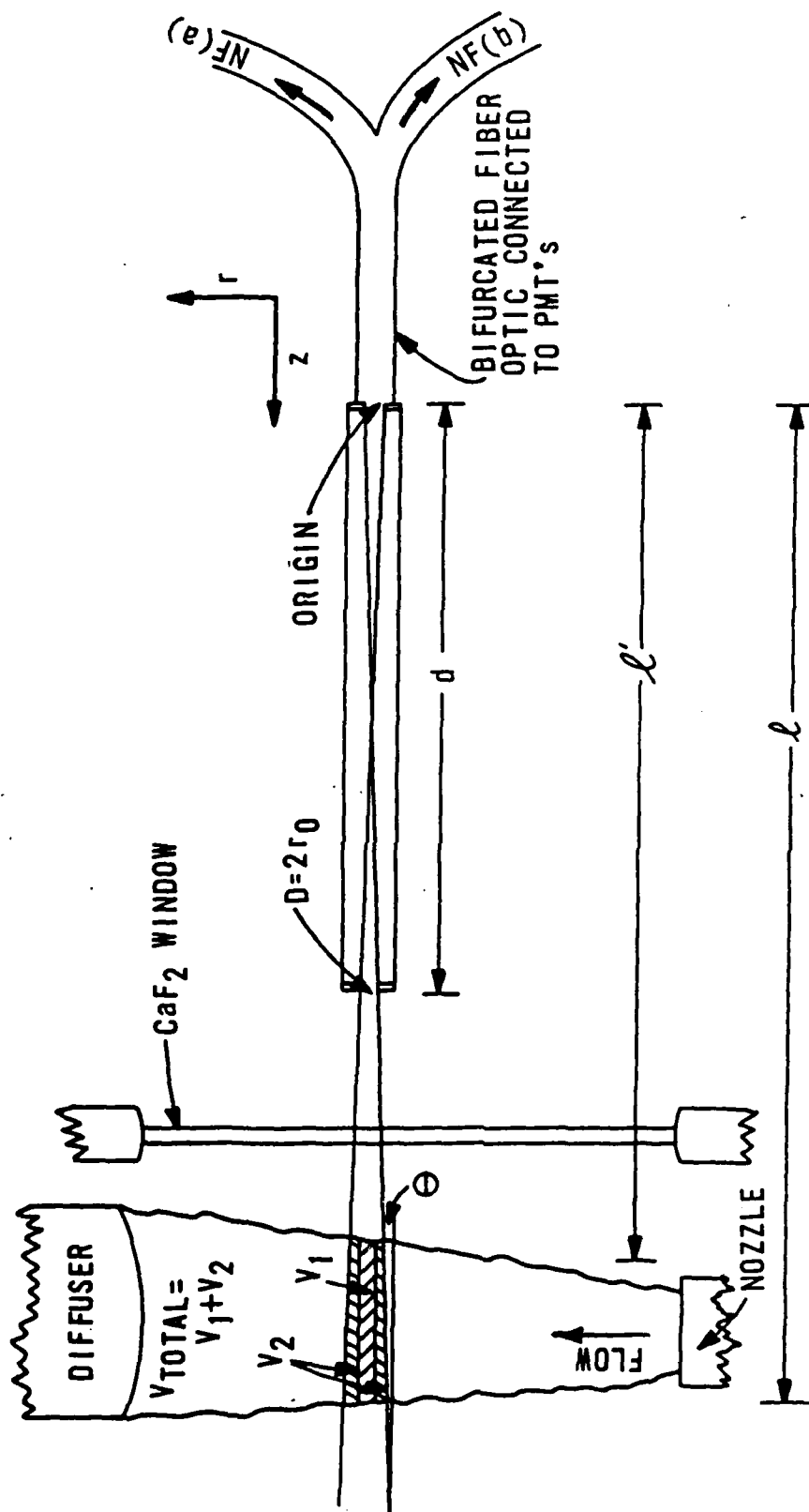


Figure 2. Experimental setup of the diagnostics.

precise collection volume along the scan (Fig. 3). Through several manipulations as given in Reference 3, the number of photons/s landing on the detector, N^* , is given by

$$N^* = \frac{P'}{h\nu} = \frac{T[NF^*]h\nu k_T A}{4\pi} \cdot \left[2\pi \int_L^L \int_0^{r_0} \frac{zr \, dzdr}{(r^2 + z^2)^{3/2}} + \pi \int_L^L \int_{r_0}^{2rz/d - r_0} \frac{zr \, dzdr}{(r^2 + z^2)^{3/2}} \right] \quad (7)$$

where T is the total transmission of any filters used in the diagnostic plus the transmission of the cavity window.

VERIFICATION OF POSSIBLE INTERFERENCES FROM CLOSE-LYING PEAKS IN THE $NF(a^1\Delta)$ DIAGNOSTIC

To determine the amount of interference from the $HF(3-0)$ emission, a moderate resolution spectra was obtained using an OMA III (EG&G PAR) with a 1200 λ/mm grating. Figure 4 shows a scan with just the combustor, used to produce F atoms, operating. It was assumed that the majority of HF^* originated from the combustor. Only the region of interest from 870 nm to 900 nm is shown. Figure 5 shows a scan with $NF(a^1\Delta)$ and $N_2(B)$ being produced. The HF distribution appears to change very little in intensity when $N_2F_4 + H_2$ is added. This comparison was made over a wide variety of N_2F_4 and secondary H_2 flows. The results were consistent within our flow conditions; therefore, a simple subtraction of the HF contribution yielded a reliable correction factor for HF .

Scans to determine the population in the $N_2(B, v' - v'') = 1 - 0, 0 - 0$ and $0 - 1$ were performed using a 0.3-m monochromator (Acton) with a 1200 λ/mm grating blazed at 1.0 μm . The monochromator was equipped with an intrinsic germanium detector (Applied Detector Corporation). The scans showed little or no interference, with our flow conditions, from the $N_2(B, 1 - 0)$ peak. The scans showed the population in the strong $0 - 0$ peak to be very low

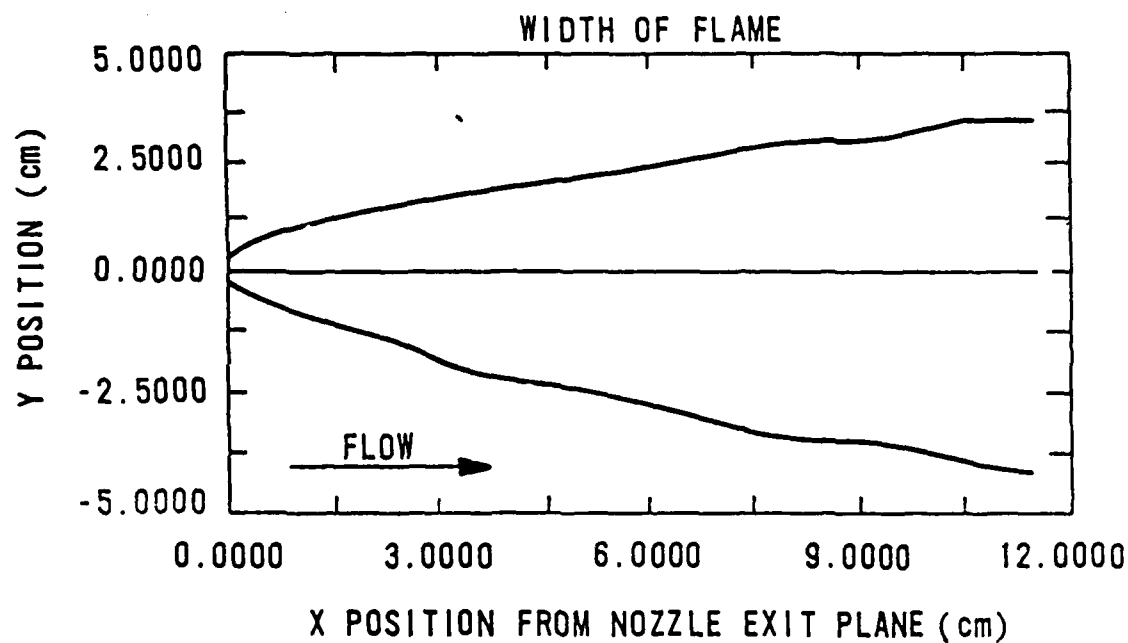


Figure 3. Digitized photograph of the actual device flame.

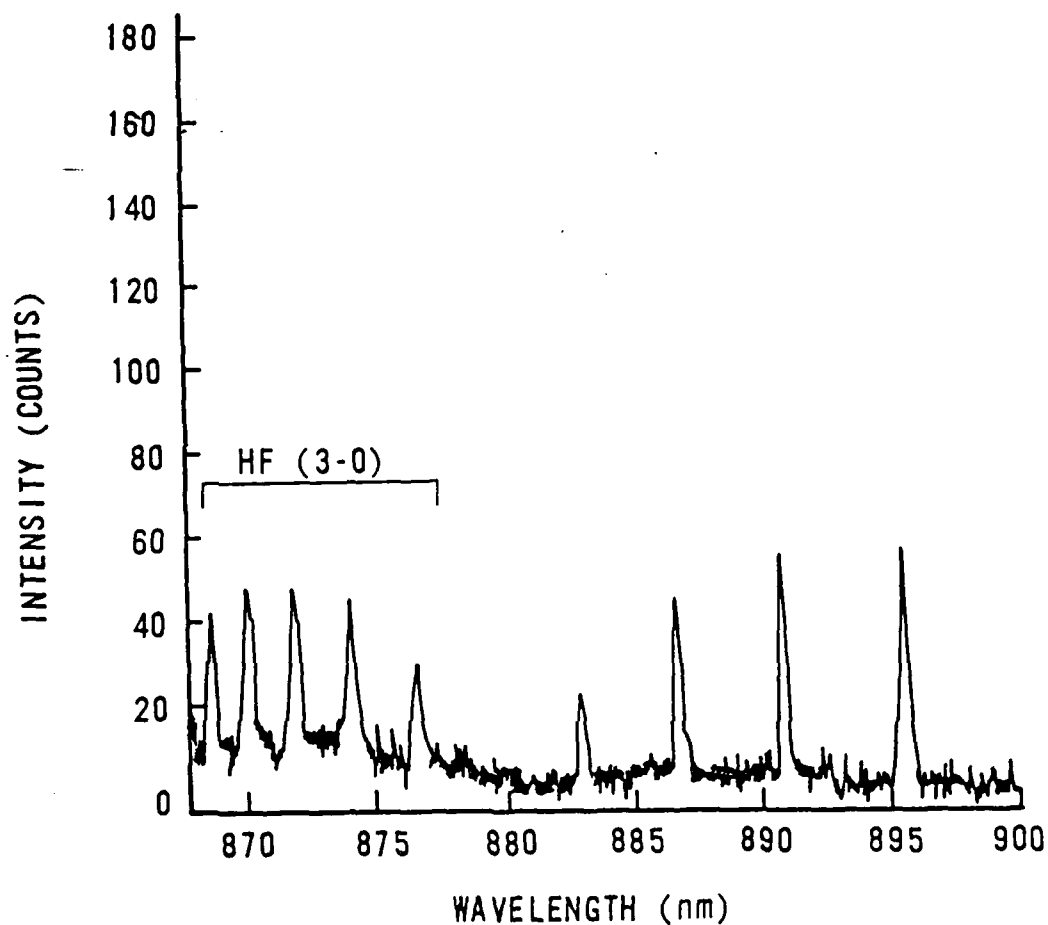


Figure 4. OMA III scan of the HF emission.

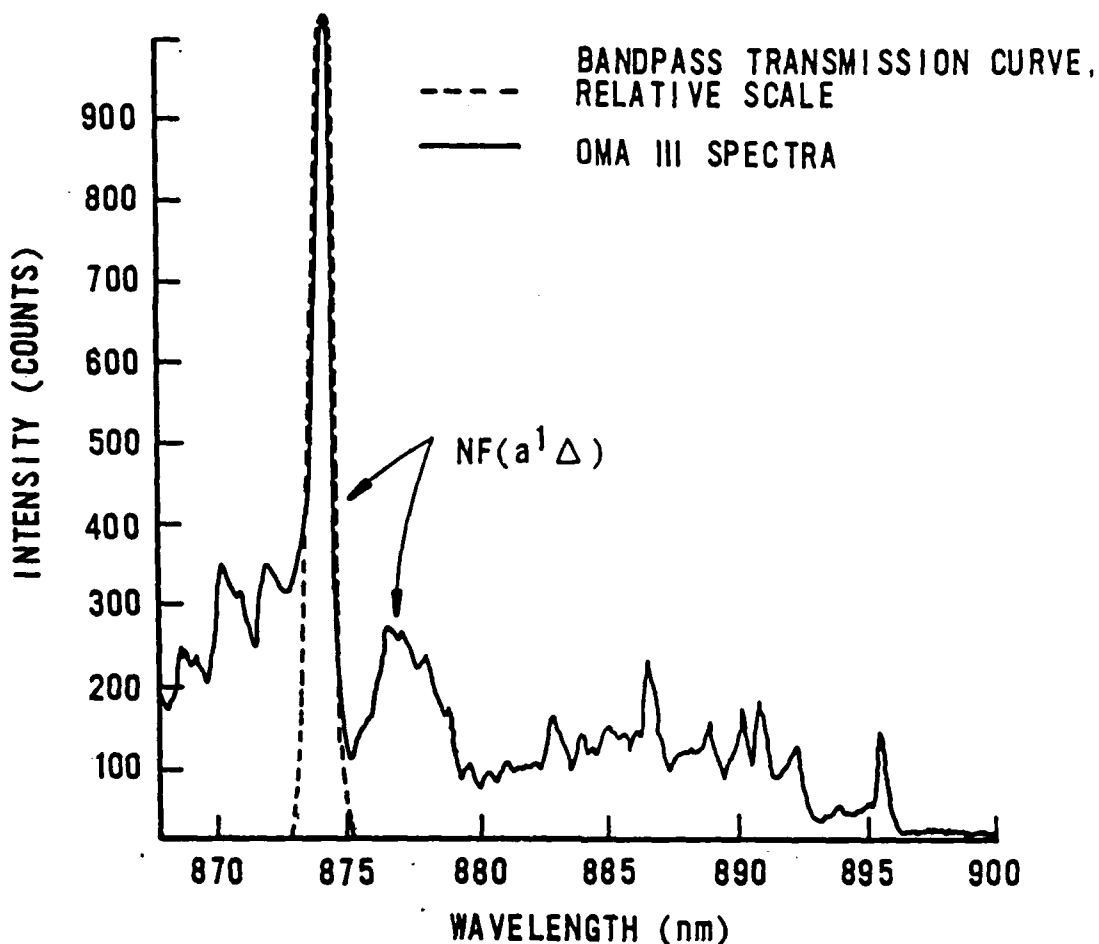


Figure 5. OMA III scan of the NF ($a^1\Delta$) and HF region with an overlay of the band-pass filter transmission curve.

(approximately 10^8 molecules/cm³), which substantiated the minimal interference from the 1 - 0 peak.

The monochromator scans allowed for a more accurate separation of the HF and NF(a) peaks as well. The result was that the HF contribution to the NF(a) diagnostic signal never exceeded 33 percent of the diagnostic signal; however, the average contribution was around 10 percent for our flow conditions. The $N_2(B)$ and HF population were monitored for each type of run condition. Therefore, the exact contribution to the NF($a^1\Delta$) diagnostic could be subtracted out. A monochromator scan with the trace of the narrow band-pass filter transmission curve is shown in Figure 6. The area under the spectral curve was multiplied by the band-pass transmission to obtain actual interferences in specific flow conditions.

--- BANDPASS FILTER TRANSMISSION CURVE

— WORST FLOW CASE
SCAN WITH 0.3m MONOCHROMATOR
500 nm BLAZED, 1200 λ /mm GRATING
50 μ SLITS

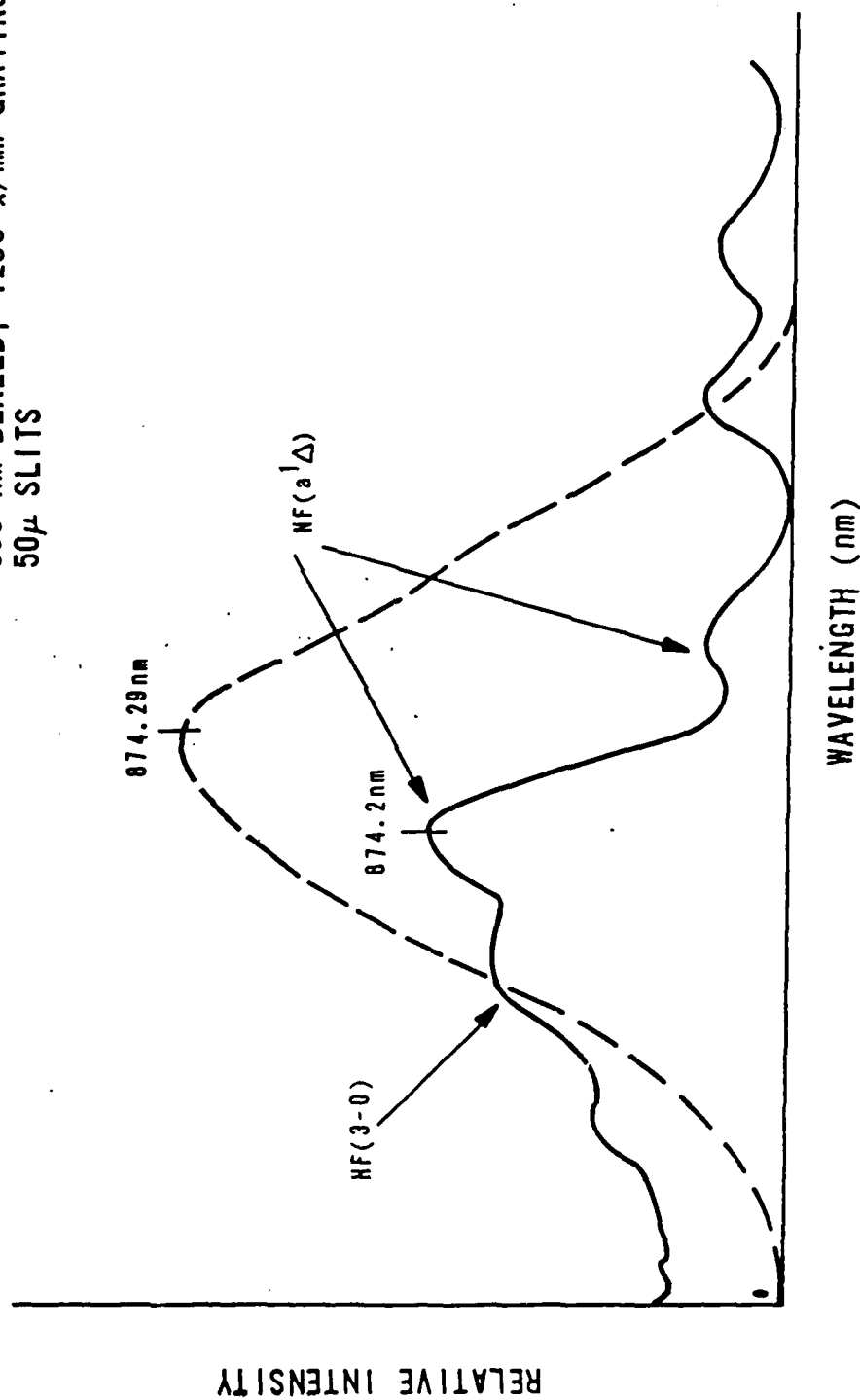


Figure 6. Monochromator scan of the NF($a'_1\Delta$) region with an overlay of the band-pass filter transmission.

IV. RESULTS

The $\text{NF}(a^1\Delta)$ and $\text{NF}(b^1\Sigma)$ diagnostics were extremely useful in determining the yield of the $\text{N}_2\text{F}_4 + \text{H}_2$ chemical production system. Figures 7 and 8 contain sample scans of the diagnostics along the centerline of the flow field. The detection capability of the $\text{NF}(a^1\Delta)$ was from 10^{14} to 10^{16} molecules/cm³ in the current arrangement, with an error of ± 20 percent. Error in determining the active volume actually sampled by the diagnostic is close to 10 percent. The errors in determining the exact ratio of interferences to the $\text{NF}(a^1\Delta)$ signal are within 10 percent. At this time there is some question as to whether the $\text{NF}(a^1\Delta)$ lifetime is correct; however, until the lifetime is verified, that error cannot be assessed. Once the lifetime is determined, the diagnostic calibration may simply be corrected. The $\text{NF}(b^1\Sigma)$ diagnostic had a range from 10^{11} to 10^{13} molecules/cm³ and an error of ± 10 percent, arising mostly from determining the geometry of the sampled volume.

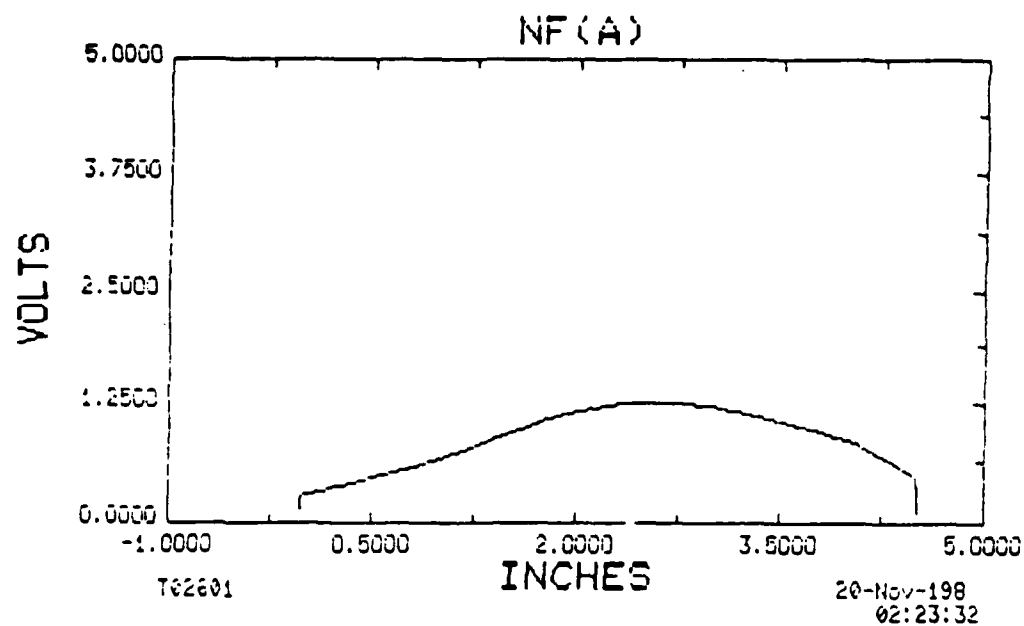


Figure 7. Sample $NF(a^1\Delta)$ scan with the diagnostic.

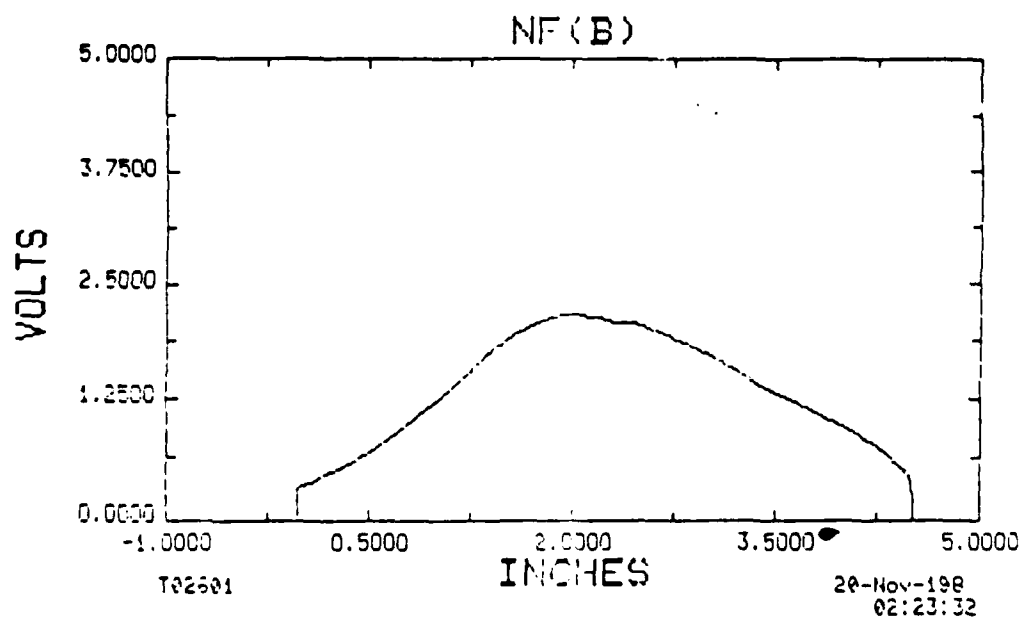


Figure 8. Sample $NF(b^1\Sigma)$ scan with the diagnostic.

V. CONCLUSIONS AND RECOMMENDATIONS

The $\text{NF}(a^1\Delta)$ and $\text{NF}(b^1\Sigma)$ diagnostics have been critical in determining the overall production of the two species as well as the species distribution across the flow field. The $\text{NF}(a^1\Delta)$ diagnostic requires in-depth analysis of the medium before application. It is especially important to determine all possible interferences from other species emission. The application of this diagnostic to the $\text{N}_2\text{F}_4 + \text{H}_2$ system led to a reexamination of the branching ratio as defined by Eqs. 3 and 4. The branching ratio is currently being investigated.

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